



Walsh, D., Sanchez-Ballester, N. M., Ting, V., Hall, S. R., Terry, L. R., & Weller, M. T. (2015). Visible light promoted photocatalytic water oxidation: Effect of metal oxide catalyst composition and light intensity. *Catalysis Science and Technology*, 5(10), 4760-4764.  
<https://doi.org/10.1039/c5cy01203a>

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# Visible light promoted photocatalytic water oxidation: effect of metal oxide catalyst composition and light intensity

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**A range of low cost nanoparticulate mixed transition metal oxides were prepared using a simple methodology and used as catalysts in visible light promoted water oxidations. The effect of catalyst and daylight equivalent light intensities on reaction efficiency in terms of O<sub>2</sub> yields, TOF and proton production was determined.**

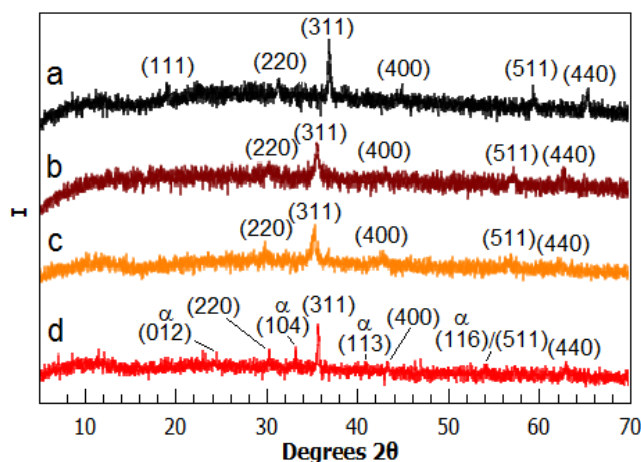
The capture and storage of energy in the form of convenient, inexpensive fuels remains technically elusive. The discovery of materials that would facilitate the efficient molecular-level energy conversion directly from sunlight, water, and possibly carbon dioxide, to fuels is a major challenge but if realized would have a revolutionary impact on our energy economy and systems. The design of practical solar-fuel generation systems with the required efficiency, scalability, and sustainability to be economically viable has clear benefits. Photosynthesis is the most important natural process on earth and artificial photosynthesis (AP) which utilizes the fundamental processes that encompass Photosystem II (PSII) water oxidation, linked to development of Photosystem I (PSI-like) systems for the complete water splitting reaction and generation of liquid fuels is an appealing approach.<sup>1,2</sup>

Water oxidation utilizes the photocycling light absorbing dye [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, together with an electron acceptor which extracts an electron from the excited state [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup> dye giving [Ru(bpy)]<sup>3+</sup>. An electron is then donated from a metal oxide catalyst to restore the stable [Ru(bpy)]<sup>2+</sup> state and absorbed water oxidized on the metal oxide surface with release of O<sub>2</sub> gas and protons.<sup>3,4</sup> In total 4 photons generate 4 protons and an O<sub>2</sub> molecule. Water oxidation forms half of the complete water splitting reaction and the ultimate aim is to derive a combined system with reduction of released protons to hydrogen or, in place of an electron acceptor, the electrons generated used for CO<sub>2</sub> reduction into solar fuels such as methanol.<sup>5,6</sup>

Previously, ruthenium or iridium metal oxides or complexes have been successfully employed as the catalyst.<sup>7-9</sup> Recently cobalt oxides or ligated cobalt complexes have been shown to be effective agents for the water oxidation reaction.<sup>10-12</sup> Similarly nickel based oxides have been shown to be effective catalysts.<sup>13,14</sup> Whilst cobalt and nickel based catalysts are less costly compared rare earth metals, these compounds are highly toxic, allergens and potent carcinogens.<sup>15,16</sup> Therefore in this work we have investigated the use of lower toxicity and low cost abundant 3d transition metals as

alternatives to act as catalysts for the visible light promoted water oxidation reaction. Together with the use of these catalysts the effect of light intensity on the water oxidation reaction rate, longevity and quantum yield ( $\phi$ ) has been investigated.

A range of spinel metal oxides were prepared using a simple combustion synthesis significantly adapted from the Pechini citric acid and glycol methodology (Table 1).<sup>17</sup> Briefly, metal nitrate salts were mixed in solution with the biopolymer dextran, ammonia solution was then added to form suspensions of the oxide. These were dried and heated very briefly to 450°C to promote a controlled combustion to readily form low density porous frameworks that ranged in colour from brick red for iron oxide through to pure black for cobalt oxide preparations (experimental details are described in the ESI†). The frameworks were composed of loosely connected nanoparticles of the metal oxides as shown by SEM (ESI† Fig.S1). Powder XRD measurements were conducted to identify the metal oxide phases obtained. These gave quite broad reflections that corresponded to low crystalline pure phase cobalt oxide as Co<sub>3</sub>O<sub>4</sub> (JCPDS 42-1467), spinel ferrite oxides of CoMn<sub>2</sub>O<sub>4</sub> (JCPDS 02-1086) and MnFe<sub>2</sub>O<sub>4</sub> (JCPDS 10-0139), and a mixed phase of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) (JCPDS 39-1346) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) (JCPDS 33-0664) (Fig. 1). A weak reflection at  $d(\text{\AA})$ 3.68 corresponding to {012} facets of hematite was present, notably this crystal face has been implicated with increased water oxidation activity in photocatalysed reactions in conjunction with [Ru(bpy)]<sup>2+</sup> sensitizer.<sup>18</sup> The UV-visible absorption spectrum of this mixed phase sample was measured and a Tauc plot of  $(ah\nu)^2$  against  $(h\nu)$  for the direct transition gave a band gap of  $\sim 1.98\text{eV}$  which corresponds to the reported value for maghemite (ESI† Fig. S2 a,b).<sup>19</sup>



**Fig. 1** Powder X-ray diffractograms of prepared metal oxides showing (a) Co<sub>3</sub>O<sub>4</sub>; (b) CoFe<sub>2</sub>O<sub>4</sub>; (c) MnFe<sub>2</sub>O<sub>4</sub>; (d)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> mixed phase.

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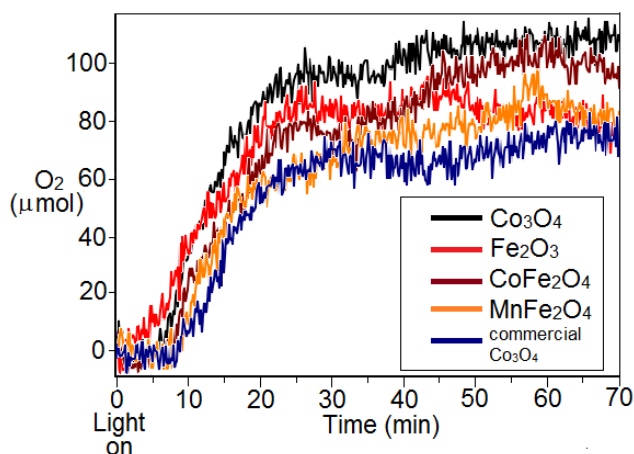
† Electronic Supplementary Information (ESI) available: Experimental details, SEM, Raman analysis, UV-vis spectrophotometry, Raman spectroscopy, TEM, XRD, example calculations. See DOI: 10.1039/x0xx00000x

Low crystallinity nanoparticles were obtained due to the low temperature and short heating methodology employed. Phase composition was confirmed by Raman spectroscopy of the samples (ESI<sup>†</sup> Fig. 3). The size and shape of the particles that compose the open framework structured formed from the combustion step were analyzed by TEM, this showed irregular spherical and cubic nanoparticles ranging from ~10-15nm for Co<sub>3</sub>O<sub>4</sub> up to irregular faceted block shaped 30nm nanoparticles for Fe<sub>2</sub>O<sub>3</sub> were formed (ESI<sup>†</sup> Fig.S4). Brunauer, Emmett and Teller (BET) surface area measurements of lightly ground samples were commensurate with the TEM observations (Table 1).

The prepared metal oxides were employed as catalysts in visible light photocatalysed water oxidations using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> light sensitizer. Persulphate has traditionally been used as an electron acceptor, however the powerful sulphate radical anion (SO<sub>4</sub><sup>•-</sup>) formed promotes oxidative decomposition of reagents, generation of CO<sub>2</sub> and shortening of reaction lifetimes.<sup>ref</sup> [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> was used as electron acceptor, though previously it has been shown that at longer reaction times cobalt oxide can be generated in-situ which can then contribute to catalytic activity.<sup>12, 20</sup> Thus rate and yield obtained within 35min of light-on was used for evaluation here. Stirred reactions were conducted in N<sub>2</sub> degassed acetate buffer, illuminated with a 3W blue led (λ<sub>max</sub> 465nm) lamp at a specific distance from the reaction flask surface to give a measured light intensity of at the outer flask surface. Release of O<sub>2</sub> and reaction mixture pH were monitored simultaneously in-situ and in real time. An optical O<sub>2</sub> sensor combined with a temperature compensation probe was used for accurate gaseous O<sub>2</sub> measurements (experimental details are described in the ESI<sup>†</sup>).



Reactions were also conducted using a commercial laser ablated sample of Co<sub>3</sub>O<sub>4</sub> (Com-Co<sub>3</sub>O<sub>4</sub>) nanopowder as comparison. Taking the maximum O<sub>2</sub> yield within the initial 35 minutes of light exposure showed that the prepared Co<sub>3</sub>O<sub>4</sub> catalyst sample gave highest yield, followed by the mixed phase Fe<sub>2</sub>O<sub>3</sub>, then the CoFe<sub>2</sub>O<sub>4</sub> sample, with the manganese ferrite MnFe<sub>2</sub>O<sub>4</sub> and commercial Co<sub>3</sub>O<sub>4</sub> giving the lowest yields.



**Fig. 2** Visible light photocatalysed water oxidations showing O<sub>2</sub> yield with time using 5mWcm<sup>-2</sup> blue light with catalyst of (a) Co<sub>3</sub>O<sub>4</sub>; (b) γ-Fe<sub>2</sub>O<sub>3</sub> and α-Fe<sub>2</sub>O<sub>3</sub>; (c) CoFe<sub>2</sub>O<sub>4</sub>; (d) MnFe<sub>2</sub>O<sub>4</sub>; (e) commercial Co<sub>3</sub>O<sub>4</sub> nanopowder.

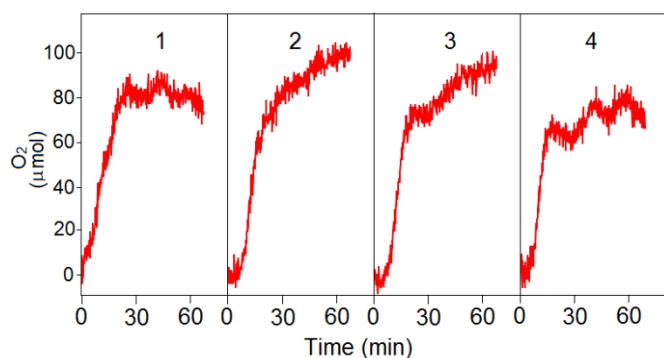
**Table 1** Maximum net O<sub>2</sub> generated and production rate (from 5-15 min), calculated TOF's (TOF as mol O<sub>2</sub> sec<sup>-1</sup>/mol (active) metal). Quantum yield ΦO<sub>2</sub>% = O<sub>2</sub> produced at t = O<sub>2max</sub><35min/photons absorbed at t= 35min × 400% (4 photons absorbed per O<sub>2</sub>). (Example calculations are shown in the ESI<sup>†</sup>).

| Sample<br>(S <sub>BET</sub> m <sup>2</sup> g <sup>-1</sup> ) | O <sub>2</sub> yield (at<br>t<35min)<br>μmol | O <sub>2</sub> (5-15min)/<br>μmol s <sup>-1</sup> | TOF <sub>max</sub><br>10 <sup>-3</sup> s <sup>-1</sup> | ΦO <sub>2</sub> % (at<br>t= 35 min) |
|--|--|---|--|-------------------------------------|
| Co <sub>3</sub> O <sub>4</sub> (61.3)                        | 98   | 0.105   | 0.843  | 31.1                                |
| Fe <sub>2</sub> O <sub>3</sub> (38.7)                        | 83   | 0.067   | 0.535  | 25.9                                |
| CoFe <sub>2</sub> O <sub>4</sub> (27.8)                      | 77   | 0.069   | 0.542  | 24.4                                |
| MnFe <sub>2</sub> O <sub>4</sub> (39.6)                      | 76   | 0.077   | 0.597  | 24.1                                |
| Com-Co <sub>3</sub> O <sub>4</sub> (35.8)                    | 70   | 0.055   | 0.442  | 22.2                                |

The highest initial Turn Over Frequency (TOF) and φ was obtained with Co<sub>4</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub> produced the second fastest rate, which was reflected in the relatively high measured surface area of this oxide. However O<sub>2</sub> generation was not as sustained as with Fe<sub>2</sub>O<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> whose O<sub>2</sub> production rates were similar (Fig. 2). It may be that the cobalt component, in particular Co<sup>3+</sup> in octahedral sites as indicated by a prominent T<sub>2g</sub> Raman Shift at ~470cm<sup>-1</sup> (Fig S3c ESI),<sup>21</sup> promotes activity disproportionate to the lower surface area of this sample.<sup>22</sup> The laser ablated commercial Co<sub>3</sub>O<sub>4</sub> gave a relatively moderate O<sub>2</sub> yield and rate in comparison. Heterogeneous catalyst activity depends on a number of factors including surface area, metal oxidation states, surface texture and favourable facets and edges. In some instances amorphous phases have been reported to be more effective, whilst in others crystal edges have been implicated in higher activity.<sup>23, 24</sup> It may be that rapid combustion with a short heating step give the low crystalline mixed phase and mixed metal oxides that are more optimal for this catalysis. This may be because the products have more numerous surface defects, edges and interfaces between conjoined nanoparticles that favour water bonding and the subsequent oxidation reaction sequence. In the case of Fe<sub>2</sub>O<sub>3</sub> several additional factors may be combining to increase O<sub>2</sub> yield. Firstly the presence of {012} facets,<sup>18</sup> also the mixed γ/α phase may allow more dynamic electronic transitions that facilitate electron transfer to the [Ru(bpy)<sub>3</sub>]<sup>3+</sup> and transient Fe<sup>3+</sup>-Fe<sup>4+</sup>-Fe<sup>3+</sup> upon oxidation of water to O<sub>2</sub> and protons.

#### Catalyst recycling

The mixed phase ferrimagnetic maghemite/ ferromagnetic hematite Fe<sub>2</sub>O<sub>3</sub> catalyst responded well to a strong magnet and could be easily collected from a completed water oxidation reaction for re-use. O<sub>2</sub> evolution profiles from four successive reactions using recovered Fe<sub>2</sub>O<sub>3</sub> as the catalyst were measured (Fig.3). This showed that the most rapid onset of O<sub>2</sub> generation occurred on initial use, thereafter an increasing lag was present. O<sub>2</sub> yields were similar for the first three successive reactions, with a moderate decrease evident upon fourth use.



**Fig. 3** Visible light photocatalysed water oxidations showing O<sub>2</sub> yield with time using 5mWcm<sup>-2</sup> blue light with 10mg co-catalyst of mixed phase Fe<sub>2</sub>O<sub>3</sub> which was recovered and re-used in a further three successive reactions.

The recovered and washed Fe<sub>2</sub>O<sub>3</sub> catalyst darkened with successive usage (ESI<sup>†</sup> Fig.S5). TEM of the sample showed the Fe<sub>2</sub>O<sub>3</sub> crystals had become decorated with nanoparticles. XRD showed the presence of a low level of Co<sub>3</sub>O<sub>4</sub>/ Co(OH)<sub>x</sub> suggesting that the accumulated surface material was nanoparticles of cobalt oxide derived from decomposed electron acceptor (ESI<sup>†</sup> Figure 6a,b). Accumulation of the cobalt oxide may account for increased lag times and fluctuations in O<sub>2</sub> output in successive reactions after the initial ~25min linear phase, due to complex interplay between cobalt oxidized to Co<sub>3</sub>O<sub>4</sub> producing high catalytic activity coupled with electron extraction from excited state Ru(bpy)<sub>3</sub><sup>2+</sup> being diverted to oxidation of cobalt hydroxide into Co<sub>3</sub>O<sub>4</sub> without O<sub>2</sub> generation.

#### Light intensity

For practical application of this approach to solar fuel production it should be able to operate at natural daylight intensities, including on overcast days and in locations at higher latitude with varying annual day length and lesser light intensity compared to equatorial regions. Our measurements have shown that (at ~51°N and 170m elevation) in direct sunlight at noon the 420-490nm light intensity varies between 5mWcm<sup>-2</sup> in December, to 9mWcm<sup>-2</sup> at spring and autumn equinox's to reach a maximum of 10.5mW cm<sup>-2</sup> in June (Fig. 4a).

The quality of light varies greatly on overcast days however, being upwards from a minimum of ~0.5mWcm<sup>-2</sup>. Therefore the effect of incoming light intensity on the water oxidation reaction was investigated. As the mixed phase Fe<sub>2</sub>O<sub>3</sub> is relatively non-toxic, highly abundant and performed well in the water oxidations it was used as the metal oxide catalyst. Recently it been reported that more complex molecular iron based water oxidation catalysts convert to Fe<sub>2</sub>O<sub>3</sub> within the reaction which then can act as the actual catalyst.<sup>25</sup> A series of water oxidation reactions was conducted using matching reaction reagents and protocol except that the blue led light impinging on the reaction flask was set to generate values ranging between 0.6 - 10mWcm<sup>-2</sup> as a match to realistic daylight levels.

Fig. 4b shows the O<sub>2</sub> release profile under increasing light intensity. O<sub>2</sub> yields and TOF were shown to be dependent on light intensity, with 10mWcm<sup>-2</sup> producing a maximum O<sub>2</sub> yield of

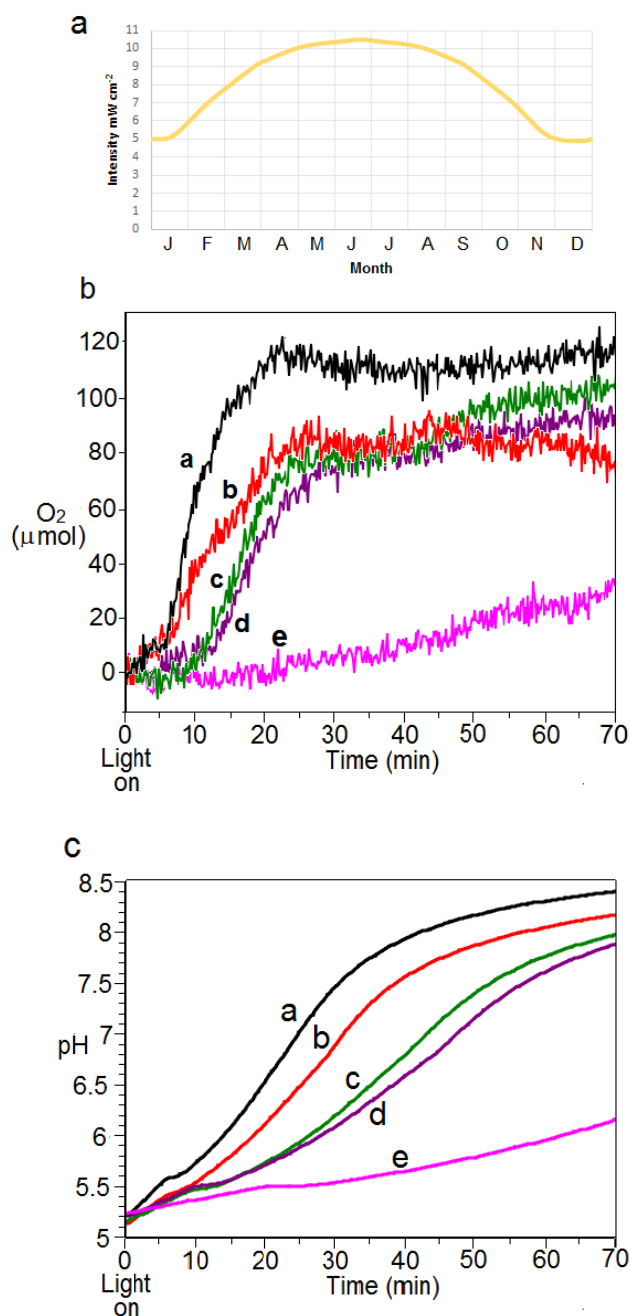
118μmol O<sub>2</sub>, close to the maximum theoretical yield of 120μmol based on electron acceptor concentration. 5mWcm<sup>-2</sup> light gave rate and O<sub>2</sub> output intermediate between the 10 and 2.5mW values. Only a marginal reduction was obtained between 2.5 to 1.3mWcm<sup>-2</sup>. Lag between light-on and onset of O<sub>2</sub> and proton production was seen to lengthen as light intensity was lowered however. Thereafter photocycling appeared to be less dependent on light intensity as reaction rates were similar. When light intensity was lowered to 0.6mWcm<sup>-2</sup> a prolonged lag phase of over 20 min. before onset of minimal activity was found, this light intensity appears to fall below the minimum level for satisfactory cyclic photocatalyzed oxidation. The more rapid onset of O<sub>2</sub> production at both 10 and 5mWcm<sup>-2</sup> suggests that initially the higher intensity is required for full light saturation of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> sensitizer (Table 2). At lower light levels the delay indicates a build-up in concentration of the excited state [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup> was required before onset of water oxidation. At higher light intensity an abrupt cessation of water oxidation appears to occur after 20-25 min, this was most likely caused by exhaustion of the electron acceptor and at 10mW also onset of decomposition of the [Ru(bpy)<sub>3</sub>]<sup>2+/3+</sup> due to elevated pH. With this Fe<sub>2</sub>O<sub>3</sub> sample the rapid pH rise and absence of a second stage of O<sub>2</sub> evolution at longer timescale suggests that Co<sub>3</sub>O<sub>4</sub> generated by oxidation of Co(OH)<sub>x</sub> from the decomposed electron acceptor contributed to O<sub>2</sub> production to this single O<sub>2</sub> generation phase observed.<sup>20</sup> Samples reacted using light intensity between 5-1.3mW showed a minor upswing in O<sub>2</sub> production from ~40min onwards, indicating that onset of activity of in-situ formed Co<sub>3</sub>O<sub>4</sub> occurred at around this point.

Fig. 4c shows the corresponding change in pH with time, reduction of the pentamine cobalt electron acceptor and release of ammonia results in the increase in pH of the buffered solution as water oxidation proceeded. An inflexion point marked the onset of O<sub>2</sub> release after between approximately 5 – 20 minutes depending on light intensity. Here a burst of proton and O<sub>2</sub> production appeared to occur which resulted in a transient levelling off of pH rise.

**Table 2** Effect of light intensity on maximum net O<sub>2</sub> generated and production rate (from 5-15 min), calculated TOF's (TOF as mol O<sub>2</sub> sec<sup>-1</sup>/mol Fe). Quantum yield ΦO<sub>2</sub>% = O<sub>2</sub> produced at t = O<sub>2max</sub> < 35min / photons absorbed at t = 35min × 400% (4 photons absorbed per O<sub>2</sub>). 10mg of mixed phase

| α/γ-Fe <sub>2</sub> O <sub>3</sub><br>Light intensity<br>(mW cm <sup>-2</sup> ) | O <sub>2</sub> yield (at<br>t<35min)<br>μmol | O <sub>2</sub> (5-<br>15min)/<br>μmol s <sup>-1</sup> | TOFmax<br>10-3 s <sup>-1</sup> | ΦO <sub>2</sub> % (at t=<br>35 min) |
|---|--|---|--------------------------------|-------------------------------------|
| 10  | 117  | 0.144   | 1.153                          | 18.5                                |
| 5   | 83   | 0.067   | 0.535                          | 25.9                                |
| 2.5   | 80   | 0.055   | 0.443                          | 50.8                                |
| 1.3   | 76   | 0.03  | 0.24                           | 92                                  |
| 0.6   | 8  | -   | -                              | 24.5                                |

Fe<sub>2</sub>O<sub>3</sub> used as catalyst in each reaction.



**Fig. 4** (a) Measured monthly maximum light intensity (over 420–490nm with clear sky at noon at 51.4°N latitude and 170m elevation); (b) photocatalysed water oxidation showing O<sub>2</sub> yield with time using 10mg of prepared mixed phase Fe<sub>2</sub>O<sub>3</sub> catalyst and (c) change in pH with time. Using blue light intensity (mW cm<sup>-2</sup>) of (a) 10; (b) 5; (c) 2.5; (d) 1.3; (e) 0.6.

## Conclusions

A simple methodology was devised using minimal energy input for the synthesis of functional metal oxide nanoparticles. The prepared catalysts low crystallinity with accessible and abundant edges may have contributed to their activity. Cobalt oxide as Co<sub>3</sub>O<sub>4</sub> was found to be most effective in terms of O<sub>2</sub> yield and TOF for the photocatalyzed water oxidations, however a mixed phase Fe<sub>2</sub>O<sub>3</sub>,

which is more desirable in terms of toxicity, was almost as efficient. This catalyst was shown to be readily collected for re-use, though gradual accumulation of surface bound nanoparticles of cobalt oxide from decomposed electron acceptor occurred.

Reactions conducted using light intensities that realistically match daylight levels showed that the water oxidation reaction successfully occurred, though with increase in lag time, down to 1.3mWcm<sup>-2</sup>. The optimum light intensity in terms of O<sub>2</sub> yield and proton production rate, whilst minimising side reactions of decomposition of light sensitizer and re-organization of the electron acceptor into a catalyst, appeared to be around 5mW cm<sup>-2</sup>. A noticeable drop off in reaction occurred between 1.3 to 0.6mWcm<sup>-2</sup>, the lowest light level appeared to be below the threshold for sufficient build-up of the excited state Ru(bpy)<sub>3</sub><sup>2+\*</sup> with only a very minimal water oxidation reaction and O<sub>2</sub> yield resulting.

Further studies on surface topology of the prepared materials and replacing the electron acceptor with a reversible electron storage mediator as a step towards solar fuel production are currently underway.

## Notes and references

We thank Dr V. Ting, Department of Chemical Engineering, University of Bath for assistance with BET measurements. This research was funded by a University of Bath departmental grant. ‡

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